



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 521 423 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **92110926.0**

(51) Int. Cl.⁵: **B41M 5/40**

(22) Date of filing: **27.06.92**

(30) Priority: **03.07.91 US 725433**
16.12.91 US 808540

(43) Date of publication of application:
07.01.93 Bulletin 93/01

(84) Designated Contracting States:
DE ES FR GB NL SE

(71) Applicant: **POLAROID CORPORATION**
549 Technology Square
Cambridge Massachusetts 02139(US)

(72) Inventor: **Mack, Jonathan M.**
575 Central Street
Boylston, MA 01505(US)
Inventor: **Sun, Kang**
170 John Rezza Drive
Attleboro, MA 02760(US)

(74) Representative: **Patentanwälte Dipl. Ing. R.**
Splanemann Dr. B. Reitzner Dipl. Ing. K.
Baronetzky
Tal 13
W-8000 München 2(DE)

(54) **Transparent thermographic recording films.**

(57) This invention provides transparent thermographic recording films which exhibit good anti-stick properties, are scratch resistant and substantially craze-free. The thermographic recording films comprise a transparent support carrying (a) a dye image-forming system comprising a di- or triarylmethane thiolactone dye precursor, an organic silver salt, a heat-fusible organic acidic material, and polyvinylbutyral as the binder; and, (b) a protective topcoat layer positioned above said dye image-forming system and comprising a water-insoluble polymeric binder, a mixture of at least two colloidal silicas having different average particle diameters in the proportion, by weight, of 1 part of silica having an average diameter of 50 nm or smaller and 0.3 to 1 part of silica particles having an average diameter no more than 40% of the larger sized silica particles, the ratio of total silica to binder being at least 3 parts per weight silica to 1 part per weight binder. One of the colloidal silicas may be a fumed colloidal silica. An organofunctional silane may be added to the protective topcoat layer or coated as a separate layer on top of the protective topcoat layer.

EP 0 521 423 A1

Background of the Invention

(1) Field of the Invention

5 The present invention relates to transparent thermographic recording films, and more specifically, it relates to a topcoat for transparent thermographic recording films which are to be imaged with a thermal printhead and which exhibit good anti-stick properties, are scratch resistant, water resistant, substantially craze-free and low in haze.

10 (2) Description of the Related Art

Color-forming di- and triarylmethane compounds possessing certain S-containing ring closing moieties, namely a thiolactone, dithiolactone or thioether ring closing moiety are disclosed in European Patent No. 250,558 and U.S. Patent No. 4,904,572. These dye precursors undergo coloration by contacting with a
 15 Lewis acid material, preferably a metal ion of a heavy metal, particularly silver, capable of opening the S-containing ring moiety to form a colored metal complex.

As disclosed in the above-cited European Patent, the ability of these dye precursors to form a colored dye almost instantaneously when contacted with Ag⁺ renders them eminently suitable for use as color formers in thermal imaging systems employing organic silver salts, such as silver behenate. In these
 20 systems, color formation is particularly efficient since it is effected by a phase change, i.e., effected by the melting of the organic silver salt to provide the Ag⁺ necessary for coloration rather than requiring a change of state.

As disclosed in European Patent No. 250,558, mentioned above, these thermographic recording films preferably include a heat-fusible organic acid material. U.S. Patent No. 4,904,572 discloses 3,5-dihydroxy-
 25 ybenzoic acid as a preferred heat-fusible organic acid.

The above described thermal color-forming system requires a thermoplastic binder, e.g. polyvinylbutyral, in order for the image-forming chemistry to function in a thermal printing environment. When imagewise heating is accomplished by means of a thermal printhead, the thermoplastic binder is in direct contact with the thermal printhead during imaging. Since thermoplastic binders soften upon the application
 30 of heat, they tend to stick to the thermal printhead during imaging.

This "sticking" interferes with the printing, adversely effects image quality, and can cause damage to the printhead.

A number of ways to prevent sticking between a binder and a thermal printhead during printing have been suggested for various thermographic recording films. Many of these employ a protective or anti-stick
 35 topcoat comprising silica over the thermographic color-forming layer. These topcoats contact the thermal printhead during imaging to prevent "sticking". Another way to prevent sticking has been to employ a surface active agent to add anti-stick properties. However, these silica containing topcoats and surface-active agents have drawbacks and/or do not perform adequately when the binder employed in the coloring system is polyvinylbutyral and the support used for the thermosensitive recording film is a transparent
 40 support.

For example, low surface energy materials such as silicone polymers exhibit good anti-stick properties. However, the useful silicone polymers are relatively low molecular weight silicone polymers which have a tendency to be migratory and thus cause problems, e.g., they transfer to the back of the film if it is rolled
 45 for storage or to the back of the adjacent film if stored in sheets. In addition, because these silicones are polymers, their properties change with changes in moisture and temperature and therefore, their performance is not consistent under all conditions.

U.S. Patent No. 4,583,103 issued April 15, 1986 and U.S. Patent No. 4,820,682 issued April 11, 1989 disclose protective topcoats for heat-sensitive recording papers containing a binder comprising silicon
 50 modified polyvinylalcohol and colloidal silica and/or amorphous silica. The above patents also disclose topcoats wherein said colloidal silica contains silica grains having an average particle size of from about 10 millimicrons (mμ) to 100 mμ (1 mμ = 1 nanometer (nm)) and the amorphous silica has primary grain size of about 10 micrometers (μm) to 30 μm (1 μm = 10³ nm). These topcoats are disclosed as providing good printing densities, resistance to various chemicals, oils and water, and anti-sticking and anti-blocking properties. In addition, the latter patent discloses the topcoat as exhibiting excellent transparency and
 55 describes it for use on a transparent base. However, the lowest level of haze reported is 16%, a level which is higher than desirable for overhead transparency (OHT) applications.

Published UK Patent Application No. 2,210,702 having a publication date of June 14, 1989 and assigned to the same assignee as the latter two patents, discloses a heat-sensitive recording material

which, when it employs a topcoat as described above, e.g., silicon modified polyvinylalcohol and colloidal silica, reports a level of haze as low as 8%.

However, when polyvinylbutyral is used as the binder for the color-forming materials of this invention, and a topcoat as described above, i.e. silicon modified polyvinylalcohol and colloidal silica, is employed to prevent sticking, there is poor adhesion between the topcoat and underlying polyvinylbutyral layer, as well as poor scratch resistance of the resulting film. In addition, the silicon modified polyvinyl alcohol binder is water soluble and can be rubbed off with water.

U.S. Patent No. 4,985,394 issued January 15, 1991 discloses a topcoat for a thermosensitive recording material which comprises at least one inorganic pigment selected from the group consisting of silica and calcium carbonate, each having an average particle diameter of 0.1 μm or less, and a water-soluble binder, formed on the thermosensitive coloring layer. Many of these topcoats have problems of inadequate transparency and/or adhesion when coated over the polyvinylbutyral color-forming layer of the present invention.

Thus, a hard, durable topcoat is required which can be placed over the polyvinylbutyral color-forming layer(s) to prevent sticking of the polyvinylbutyral to the thermal printhead during printing, and which is resistant to scratching and crazing and also exhibits high transparency.

Summary of the Invention

The present invention provides transparent thermographic recording films which exhibit good resistance to sticking during printing, are resistant to scratching and crazing and which have excellent transparency, and good wet rub resistance.

The thermographic recording films of the present invention employ a transparent support; a color-forming component comprising a thiolactone dye precursor, an organic silver salt, a heat-fusible organic acidic material and polyvinylbutyral as the binder; and, a transparent, anti-stick topcoat layer comprising a mixture of at least two colloidal silicas having different average particle diameters in the proportion, by weight, of 1:part of silica having an average diameter of 50 nm or smaller and 0.3 to 1 part of silica particles having an average diameter no more than 40% of the larger sized silica particles, the ratio of total silica to binder being at least 3 parts per weight silica to 1 part per weight binder.

One of the colloidal silicas may be a fumed colloidal silica having an average particle diameter in the range of 14-30 nm, preferably 14-15 nm.

The thermographic recording materials according to the present invention may additionally comprise an organofunctional silane in said topcoat layer or added as a separate layer on top of said topcoat layer.

Detailed Description of the Invention

The transparent thermographic recording films according to this invention comprise a transparent support carrying:

- (a) a dye image-forming system comprising a di- or triarylmethane thiolactone dye precursor, an organic silver salt, a heat-fusible organic acidic material, and polyvinylbutyral as the binder; and,
- (b) a protective topcoat layer positioned above said dye image-forming system and comprising a water-insoluble polymeric binder, a mixture of at least two colloidal silicas having different average particle diameters in the proportion, by weight, of 1 part of silica having an average diameter of 50 nm or smaller and 0.3 to 1 part of silica particles having an average diameter no more than 40% of the larger sized silica particles, the ratio of total silica to binder being at least 3 parts per weight silica to 1 part per weight binder.

One of the colloidal silicas employed in the present invention may be a fumed colloidal silica. Fumed colloidal silica is branched, three-dimensional, chain-like agglomerates of silicon dioxide. The agglomerates are composed of many primary particles which have fused together. Fumed silica is produced by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen. The fumed colloidal silica is referred to as "fumed" silica because of its smoke-like appearance as it is formed. If fumed colloidal silica is employed, an average particle diameter in the range of 14-30 nm is generally used, preferably 14-15 nm.

Silicas having an average diameter of 50 nm or less are required to be used in the present invention. Employing silicas having an average diameter in excess of 50 nm results in inferior transparent thermographic recording films having higher levels of haze and hence films which are not as transparent. For OHT applications, it is desired that the thermographic recording films have a measured level of haze less than 10%, and preferably less than 5%. It is preferred that the largest sized colloidal silica employed in the present invention be at least 20 nm in diameter, unless fumed colloidal silica is used as the largest sized

silica in which case, it is preferred that the fumed colloidal silica be at least 14 nm in diameter.

The mixture of silicas is required to give the hardness and durability necessary to prevent sticking of the polyvinylbutyral to the thermal printhead, to inhibit scratching on the surface of the thermographic recording film and to limit crazing, i.e., cracking on the surface of the film.

If only one silica of a specified average diameter is used in the present invention, the problems mentioned earlier occur. That is, if only silicas having an average diameter of the larger said silicas specified by this invention are employed, e.g., an average diameter of 50 nm, a topcoat of inadequate hardness and durability is obtained. The resulting thermographic recording film is more susceptible to scratching e.g., by fingernails and/or by the thermal printhead, and to gouging.

Employing only one silica having an average diameter of one of the smaller sized silica specified by this invention, e.g., 5 nm, results in a hard, scratch-resistant topcoat; however, it exhibits a high level of crazing.

A preferred topcoat of the present invention is one wherein the largest sized colloidal silica is a fumed colloidal silica having an average particle diameter in the range of 14-30 nm, preferably 14-15 nm. The fumed colloidal silica, because of its networked structure, has the advantage of tight packing with the smaller sized silica, e.g. 5 nm colloidal silica, to give a tough, non-gouging, crack-resistant surface. In addition, the tighter packed, networked structure results in superior print quality by reducing gouging, decreasing chatter and enhancing the scratch resistance during printing of the image relative to recording films which do not employ fumed colloidal silica. However, fumed colloidal silica imparts somewhat more haze to the system when compared with the other colloidal silicas as specified according to the present invention.

Fumed colloidal silica has been found to be particularly preferred for use with thermal printers such as Model TDU 850 commercially available from Raytheon Company, Submarine Signal Division, Portsmouth, Rhode Island.

Another preferred topcoat of this invention comprises a mixture of 3 different sized colloidal silica particles in the proportion by weight of 1 part silica particles having an average diameter of 50 nm or smaller, and 0.2 to 0.6 part of silica particles having an average diameter of no more than 40% of the larger sized silica particles, and 0.2 to 0.6 part of silica particles having an average diameter no larger than 8 nm. A particularly preferred topcoat comprises a mixture of 1 part silica having an average diameter of 50 nm, 0.6 part of silica having an average diameter of 20 nm and 0.6 part of silica having an average diameter of 5 nm.

Water-insoluble binders are required in the topcoats of the present invention. If water-soluble binders, e.g. polyvinylalcohol (PVA) and silicon modified PVA, are employed in the topcoats, there is poor adhesion between the topcoat and polyvinylbutyral color-forming layers. This results in inadequate scratch-resistance and in extreme cases, allows the two layers to be peeled apart from each other.

The water-insoluble binders for use in the present invention include aliphatic polyurethanes, styrene-maleic anhydride copolymers, polyacrylic acid, polyacrylic latex emulsions, polyvinylidene chloride copolymer emulsions and styrene-butadiene copolymer emulsions. A single binder or a combination of one or more binders can be employed.

To prevent interaction of the components in the topcoat layer with those in the solvent soluble color-forming layer beneath it, and to ameliorate the environmental concerns associated with coating from solvents, the topcoats of this invention are preferably coated out of aqueous systems. Since the binders employed are water-insoluble, they are either coated as latex emulsions or they are made water soluble by mixing with alkali, preferably aqueous ammonia which is lost upon drying. After drying, the resulting water-insoluble topcoat is advantageous in that it has enhanced wet rub resistance.

The ratio of total silica to binder, by weight, is preferably in the range of 3:1 to 15:1 silica to binder and is more preferably 4:1 to 5:1. If the ratio is smaller than 3:1, there is too little silica present so that some sticking occurs. However, if the silica to binder ratio exceeds about 15:1, the thermal sensitivity of the color-forming layer may be decreased.

The coating amount of the protective topcoat layer is in the range of about 100 to 250 mg/ft².

The colloidal silicas used in the present invention are produced commercially and are an aqueous colloidal dispersion of sub-micron sized silica particles in the form of tiny spheres of a specified average diameter. Preferably, the colloidal silicas are aqueous alkaline dispersions, e.g., ammonia stabilized colloidal silica. The fumed colloidal silicas used in the present invention are aqueous dispersions of fumed colloidal silica commercially available under the name Cab-O-Sperse® from Cabot Corporation, Cab-O-Sil Division, Tuscola, IL. Colloidal silicas and fumed colloidal silicas low in sodium content are preferred since sodium can cause corrosion of the thermal printhead.

The protective topcoat may contain an organofunctional silane having the formula $\text{RSi}(\text{OH})_3$ wherein R

represents a nonhydrolyzable organofunctional group. Alternatively, an organofunctional silane may be added as a separate layer on top of the protective layer. Preferably, an organofunctional silane is employed when fused colloidal silica is utilized in the topcoat. The organofunctional silane contains reactive silanol groups that can bond to the silica in the topcoat, while the R group is chosen so that it will covalently bond to pendant organofunctional groups on the polymeric binder used in the topcoat. Thus, the organofunctional silane is added to react with both the silica and binder(s) in the topcoat, functioning as a coupling agent to join the two and thereby reinforce and strengthen the silica/polymeric binder matrix. This reinforced silica/polymeric binder matrix improves the scratch resistance of the recorded image and helps to reduce head build-up. Head build-up occurs when components in the topcoat adhere to and build up on the thermal printhead during printing. Head build-up can cause damage to both the image and to the thermal printhead.

As mentioned above, the organofunctional silane is selected so that it will form a stable covalent bond with the chosen polymeric binder in the protective topcoat layer. For example, if the polymeric binder contains pendant carboxylic acid groups, an organofunctional silane containing an amino functionality would be a good choice since the two will react covalently to form an amide. If the polymeric binder contains pendant hydroxy or urethane groups, an organosilane containing an epoxy functionality would be a suitable choice to form a covalent bond.

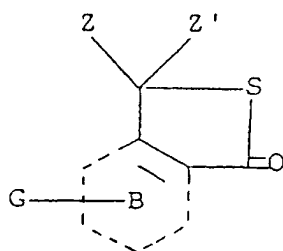
The organofunctional silane is added to the topcoat or coated as a separate overcoat layer as an aqueous dispersion. The amount of organofunctional silane employed is calculated to yield a coating coverage in the range of 5-30 mg/ft² after drying.

When the organofunctional silane is added in with the topcoat, it can be added in its hydrolyzed form, represented by RSi(OH)_3 or in an unhydrolyzed form, represented by RSi(X) , wherein R is a nonhydrolyzable organofunctional group and X is a hydrolyzable group that may be an alkoxy, acyloxy, amine or chlorine group. Preferably, X is an alkoxy group. When added in its unhydrolyzed form, X is hydrolyzed in situ to form RSi(OH)_3 .

The protective topcoat may contain other additives provided the additives do not hinder the anti-stick function of the topcoat layer, do not damage the printhead or otherwise impair image quality. Such additives include lubricants, e.g., waxes, polymeric fluorocarbons and metal soaps; surfactants, preferably nonionic surfactants and more preferably nonionic fluorosurfactants; plasticizers; anti-static agents; and ultraviolet absorbers.

The transparent supports that can be used in the present invention may be comprised of various materials and numerous suitable support substrates are known in the art and are commercially available. Examples of materials suitable for use as support substrates include polyesters, polycarbonates, polystyrenes, polyolefins, cellulose esters, polysulfones and polyimides. Specific examples include polypropylene, cellulose acetate, and most preferably, polyethylene terephthalate. The thickness of the support substrate is not particularly restricted, but should generally be in the range of about 2 to 10 mils. The support substrate may be pretreated to enhance adhesion of the polymeric coating thereto.

The di- and triarylmethane thiolactone compounds used as the dye precursors in the present invention may be represented by the formula



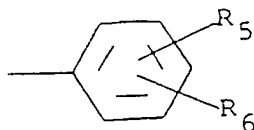
wherein ring B represents a substituted or unsubstituted carbocyclic aryl ring or rings, e.g., of the benzene or naphthalene series or a heterocyclic ring, e.g., pyridine or pyrimidine; G is hydrogen or a monovalent radical; and Z and Z' taken individually represent the moieties to complete the auxochromophoric system of a diarylmethane or a triarylmethane dye when said S-containing ring is open and Z and Z' taken together represent the bridged moieties to complete the auxochromophoric system of a bridged triarylmethane dye when said S-containing ring is open, i.e., when the ring sulfur atom is not bonded to the meso carbon atom. Usually, at least one of Z and Z' whether taken individually or together possesses as an auxochromic substituent, a nitrogen, oxygen or sulfur atom or a group of atoms containing nitrogen, oxygen or sulfur.

In the triarylmethane compounds represented in formula I above, the moieties Z and Z', when taken

individually, may be the same or different and typically represent heterocyclic groups containing nitrogen, oxygen or sulfur as the heterocyclic atom, particularly N-heterocyclic groups such as julolidin-3-yl, indol-3-yl, pyrrol-2-yl, carbazol-3-yl, and indolin-5-yl wherein the N atom of the indolyl, pyrrol, carbazolyl and indolinyl groups may be substituted with hydrogen or alkyl having 1 to 6 carbon atoms, or the moieties Z and Z' typically may be carbocyclic aryl, particularly phenyl or naphthyl groups which include an appropriately positioned auxochromic substituent, i.e., an atom or group that produces an auxochromic effect, which substituent is usually positioned para to the meso carbon atom. Typically, Z and Z' when taken together represent aryl groups bridged by a heteroatom, such as, oxygen, sulfur or nitrogen to form, for example, 4H-chromeno [2,3-C] pyrazole and particularly represent carbocyclic aryl groups, such as, phenyl groups bridged with a heteroatom, preferably oxygen, sulfur or nitrogen substituted with hydrogen or an alkyl group having 1 to 6 carbon atoms to provide a xanthene, thioxanthene or an acridine dye, which dyes possess an auxochromic substituent(s) para to the meso carbon atom, i.e., in the 3-position or in the 3,6-positions or meta and para to the meso carbon atom, i.e., in the 3,7-positions.

In the diarylmethane compounds, one of Z and Z' may be a heterocyclic group or carbocyclic aryl group as discussed above and the other of Z and Z' may be, for example, phenoxy, thiophenoxy, alkoxy containing 1 to 20 carbon atoms, alkylthio containing 1 to 20 carbon atoms, -N,N-(disubstituted)amino wherein each said substituent may be alkyl containing 1 to 20 carbon atoms, carbocyclic aryl containing 6 to 12 carbon atoms, aralkyl containing 7 to 15 carbon atoms particularly phenyl- and naphthyl-substituted alkyl or alkaryl containing 7 to 15 carbon atoms particularly alkyl-substituted phenyl and naphthyl. Representative alkyl groups include methyl, butyl, hexyl and octadecyl and representative aryl groups include phenyl and naphthyl. Representative alkaryl groups include p-octylphenyl, o-methylnaphthyl and p-hexylphenyl, and representative aralkyl groups include phenethyl, benzyl and naphthylmethyl.

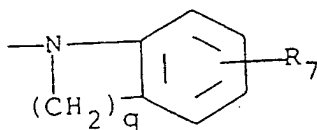
Examples of useful auxochromic substituents include -OR₁ wherein R₁ is hydrogen, alkyl usually having 1 to 6 carbon atoms, aralkyl usually having 7 to 15 carbon atoms, alkaryl usually having 7 to 15 carbon atoms or carbocyclic aryl usually having 6 to 12 carbon atoms; -SR₂ wherein R₂ has the same meaning given for R₁; -NR₃R₄ wherein R₃ and R₄ each represent hydrogen, alkyl usually having 1 to 6 carbon atoms, β -substituted ethyl, cycloalkyl usually having 5 to 7 carbon atoms, aralkyl usually having 7 to 15 carbon atoms, alkaryl usually having 7 to 15 carbon atoms or



35

wherein R₅ and R₆ each are hydrogen, alkyl usually having 1 to 6 carbon atoms, halo such as chloro, bromo, fluoro and iodo, nitro, cyano, alkoxy carbonyl wherein said alkoxy has 1 to 6 carbon atoms, sulfonamido (-NHSO₂R₀), sulfamoyl (-SO₂NHR₀), sulfonyl (-SO₂R₀), acyl (-COR₀) or carbamyl (-CONR₀) wherein R₀ usually is alkyl having 1 to 20 carbon atoms, benzyl or phenyl and R₃ and R₄ taken together represent the atoms necessary to complete a heterocyclic ring usually piperidino, pyrrolidino, N-methylpiperidino, morpholino or

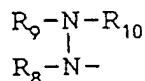
45



50

wherein q is an integer 2 to 5 and R₇ has the same meaning as R₅.

55



wherein R₈ and R₉ each are hydrogen, alkyl usually having 1 to 6 carbon atoms or



5

wherein R_{11} and R_{12} have the same meaning as R_5 and R_6 and R_{10} is $-\text{COR}_{13}$, $-\text{CSR}_{13}$ or $-\text{SO}_2\text{R}_{13}$ wherein R_{13} is hydrogen, alkyl usually having 1 to 6 carbon atoms, phenyl, $-\text{NH}_2$, $-\text{NHR}_{14}$, $-\text{N}(\text{R}_{14})_2$ or $-\text{OR}_{14}$ wherein R_{14} is hydrogen, alkyl usually containing 1 to 6 carbon atoms or phenyl. Representative alkyl groups include methyl, ethyl, propyl, butyl and hexyl. Representative β -substituted ethyl groups include β -methoxymethoxyethyl and β -2'-tetrahydropyranloxyethyl. Representative aralkyl groups include phenyl and naphthyl-substituted alkyl, such as, benzyl, phenethyl and naphthylmethyl and representative alkaryl groups include alkyl-substituted phenyl and naphthyl, such as, o-methylphenyl, o-methylnaphthyl and p-hexylphenyl. Representative carbocyclic aryl groups include phenyl and naphthyl and representative cycloalkyl groups include cyclopentyl, cyclohexyl and cycloheptyl. It will be appreciated that the auxochromic substituent(s) will be selected for a given diarylmethane, triarylmethane or bridged triarylmethane compound to provide the desired chromophore color upon opening of the S-containing ring and to achieve facile color formation.

In addition to the auxochromic substituents, the subject dye precursor compounds may possess one or more additional substituents on Z and/or Z' and/or ring B as may be desired that do not interfere with the intended utility for the dye. Typical substituents for Z and/or Z' and for G include carboxy; hydroxy; cyano; thiocyno; mercapto; sulfo; nitro; sulfonamido ($-\text{NHSO}_2\text{R}_0$); sulfamoyl ($-\text{SO}_2\text{NHR}_0$); sulfonyl ($-\text{SO}_2\text{R}_0$); acyl ($-\text{COR}_0$); carbamyl ($-\text{CONR}_0$); halomethyl such as trifluoromethyl; alkyl usually having 1 to 20 carbon atoms such as methyl, octyl, hexadecyl; alkoxy usually having 1 to 20 carbon atoms such as methoxy, ethoxy, propoxy and butoxy; alkoxycarbonyl having 1 to 20 carbon atoms such as ethoxy- and dodecyloxycarbonyl; aralkyl usually having 7 to 15 carbon atoms, for example, phenyl- or naphthyl-substituted alkyl such as benzyl, phenethyl and naphthylmethyl; alkaryl usually having 7 to 15 carbon atoms, for example, alkyl substituted phenyl or naphthyl such as o-methylphenyl, o-methylnaphthyl and p-hexylphenyl; aralkyloxy usually having 7 to 15 carbon atoms, for example, phenyl- or naphthyl-substituted alkoxy such as benzyloxy, phenethyloxy and naphthylmethyloxy; aryloxy usually containing 6 to 12 carbon atoms such as phenoxy and naphthoxy; thioalkyl groups, usually having 1 to 20 carbon atoms such as methylthio, ethylthio and hexylthio; thioaryl and thioaralkyl groups containing up to 15 carbon atoms such as phenylthio, naphthylthio, benzythio and phenethylthio; halo such as chloro, bromo, fluoro and iodo; amino including mono- and disubstituted amino such as $-\text{NR}_{15}\text{R}_{16}$ wherein R_{15} and R_{16} each are hydrogen, alkyl usually having 1 to 20 carbon atoms, aralkyl usually having 7 to 15 carbon atoms and aryl having 6 to 12 carbon atoms; and a fused substituent such as a fused benzene ring.

In a preferred embodiment, B is a benzene ring and Z and Z' taken individually or together complete the auxochromophoric system of a triarylmethane dye.

The dye precursor compounds used in the present invention can be monomeric or polymeric compounds. Suitable polymeric compounds are those which, for example, comprise a polymeric backbone chain having dye precursor moieties attached directly thereto or through pendant linking groups. Polymeric compounds of the invention can be provided by attachment of the dye precursor moiety to the polymeric chain via the Z and/or Z' moieties or the ring B. For example, a monomeric dye precursor compound having a reactable substituent group, such as an hydroxyl or amino group, can be conveniently reacted with a mono-ethylenically unsaturated and polymerizable compound having a functional and derivatizable moiety, to provide a polymerizable monomer having a pendant dye precursor moiety. Suitable mono-ethylenically unsaturated compounds for this purpose include acrylyl chloride, methacrylyl chloride, methacrylic anhydride, 2-isocyanatoethyl methacrylate and 2-hydroxyethyl acrylate, which can be reacted with an appropriately substituted dye precursor compound for production of a polymerizable monomer which in turn can be polymerized in known manner to provide a polymer having the dye precursor compound pendant from the backbone chain thereof.

The thiolactone dye precursors can be synthesized, for example, from the corresponding lactones by heating substantially equimolar amounts of the lactone and phosphorus pentasulfide or its equivalent in a suitable solvent. The silver behenate may be prepared in a conventional manner using any of various procedures well known in the art.

The organic silver salts which can be employed in the color-forming system of the present invention include silver salts of long chain aliphatic carboxylic acids such as silver laurate, silver myristate, silver

palmitate, silver stearate, silver arachidate and silver behenate; silver salts of organic compounds having an imino group such as benzotriazole silver salt, benzimidazole silver salt, carbazole silver salt and phthalazinone silver salt; silver salts of sulfur containing compounds such as S-alkylthioglycollates; silver salts of aromatic carboxylic acids such as silver benzoate and silver phthalate; silver salts of sulfonic acids such as silver ethanesulfonate; silver salt of sulfinic acids such as silver o-toluenesulfinate; silver salts of phosphoric acids such as silver phenylphosphate; silver barbiturate; silver saccharate; silver salts of salicylaldehyde; and any mixtures thereof. Of these compounds, silver salts of long chain aliphatic carboxylic acids are preferred and particularly, silver behenate which may be used in admixture with other organic silver salts if desired. Also, behenic acid may be used with the silver behenate.

The preparation of such organic silver salts is generally carried out by processes which comprise mixing a silver salt forming organic compound dispersed or dissolved in a suitable liquid with an aqueous solution of a silver salt such as silver nitrate or a silver complex salt. Various procedures for preparing the organic silver salts are described in U.S. Patents Nos. 3,458,544, 4,028,129 and 4,273,723.

The heat-fusible organic acidic material which can be employed in this invention is usually a phenol or an organic carboxylic acid, particularly a hydroxy-substituted aromatic carboxylic acid, and is preferably 3,5-dihydroxybenzoic acid. A single heat-fusible organic acid can be employed or a combination of two or more may be used.

The present invention is illustrated by the following specific examples. Examples 1-4 represent recording elements prepared by coating various topcoat formulations according to the present invention over the identical imaging system. Examples 5-9 represent comparative topcoat formulations coated over the imaging system used in Examples 1-4. Examples 10-12 represent additional recording elements prepared by coating topcoat formulations containing fumed colloidal silica according to the present invention over the same imaging system used in the previous eight examples.

The imaging system employed in each of the examples was prepared by coating Layer One onto a transparent 2.65 mil polyethylene terephthalate substrate pretreated with a solvent adherable subcoat (ICI 505, commercially available from ICI Americas, Inc., Wilmington, DE) by the slot method, followed by air drying. Layer Two was then coated on top of Layer One in the same manner and air dried. It will be appreciated that while slot coating was employed, any appropriate coating method could be used, e.g. spray, air knife, silkscreen or reverse roll. Both Layer One and Layer Two were coated from a solvent mixture comprised of 80% of methyl ethyl ketone and 20% of methyl phenyl ketone. The amounts of components used in each of the layers were calculated to give, after drying, the indicated coated coverages.

Layer One:	
	Coverage (mg/ft ²)
Polyvinylbutyral	300
Silver behenate dispersion (in polyvinylbutyral)	120 (as silver behenate)
3,5-Dihydroxybenzoic acid	54
3,5-Diisopropylsalicylic acid	4

Layer Two:Coverage (mg/ft²)

Polyvinylbutyral
(Butvar B-76, available from
Monsanto, St. Louis, Mo.)

150

Blue Dye Precursor

1

Red Dye Precursor

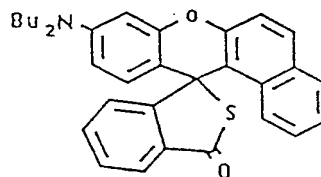
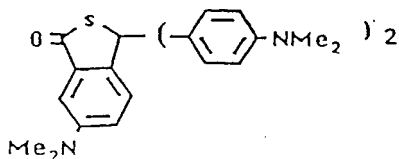
5

Black Dye Precursor

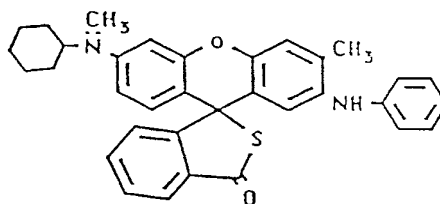
40

Blue Dye Precursor

Red Dye Precursor



Black Dye Precursor



Each of the following Examples describes a topcoat formulation which was prepared and coated, either as an aqueous dispersion or as an aqueous solution, over the above described imaging system. The amounts of components used in each topcoat formulation were calculated to give the indicated coated coverages.

Example 1

	Coverage (mg/ft ²)
NeoRez R966 Polyurethane Latex (33% total solids (TS), available from ICI Resins, Wilmington, MA)	23
Nyacol 5050, 50 nm Silica dispersion (50% TS, available from Nyacol products, Inc., Ashland, MA)	54
Nalco 2327, 20 nm Silica dispersion (40% TS, available from Nalco Chemical Co., Naperville, IL)	31
Nalco 2326, 5 nm Silica dispersion (17% TS, available from Nalco Chemical Co.)	31
Hostafon 5032, polytetrafluoroethylene dispersion, (60% TS, available from Hoechst-Celanese, Chatham, NJ)	15
Zonyl FSN, perfluoroalkyl polyethylene oxide non-ionic surfactant available from DuPont, Wilmington, DE)	6

Example 2

	Coverage (mg/ft ²)
Scripset 540 (a half ester of styrene maleic anhydride copolymer in a 5% NH ₃ , available from Monsanto, St. Louis, MO)	20
Carboset 526 (a carboxylated acrylic copolymer in NH ₃ , available from BF Goodrich, Cleveland, OH)	10
Nyacol 5050, 50 nm silica	110
Nalco 2327, 20 nm silica	20
Nalco 2326, 5 nm silica	20
Hostafon 5032	20
Zonyl FSN	8

Example 3

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nalco 2327, 20 nm silica	110
Nalco 2326, 5 nm silica	40
Hostafon 5032	10
Zonyl FSN	5

Example 4

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nyacol 5050, 50 nm silica	110
Nalco 2327, 20 nm silica	20
Nalco 2326, 5 nm silica	20
Zonyl FSN	5

Example 5

A recording element was prepared according to example 4, above, and was subsequently coated with an aqueous oligomeric aminosilane solution, commercially available under the tradename Hydrosil® 2627, from Hüls America, Inc., Bristol, PA and dried at 145° F (~63° C) to yield a coated coverage of 5 mg/ft².

Example 6

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nalco 2326, 5 nm Silica	150
Hostaflon 5032	20
Zonyl FSN	8

Example 7

	Coverage (mg/ft ²)
Scripset 540	30
Nalco 2327, 20 nm silica	150
Hostaflon 5032	20
Zonyl FSN	8

Example 8

	Coverage (mg/ft ²)
NeoRez R966	20
Nalco 2326, 5 nm silica	160
Hostaflon 5032	20
Zonyl FSN	12

Example 9

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nyacol 9950, 100 nm Silica	150
Hostaflon 5032	20
Zonyl FSN	8

Example 10

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nyacol 9950, 100 nm silica	110
Nalco 2327, 20 nm silica	20
Nalco 2326, 5 nm silica	20
Hostaflon 5032	20
Zonyl FSN	8

Example 11

	Coverage (mg/ft ²)
Scripset 540	20
Carboset 526	10
Nalco 2326, 5 nm silica	80
Cab-O-Sperse A205 (a fumed colloidal silica having an average particle diameter of 14 nm, available from Cabot Corporation, Cab-O-Sil Division, Tuscola, IL)	70
Hostafon 5032	10
Zonyl FSN	5

Example 12

Scripset 540	20
Carboset 526	10
Nalco 2326, 5 nm silica	80
Cab-O-Sperse A205	70
Hostafon 5032	10
Zonyl FSN	5
γ -Aminopropyltriethoxysilane (available from Hüls America, Inc., Bristol, PA)	5

Example 13

Scripset 540	24
Carboset 526	12
Nalco 2326, 5 nm silica	96
Cab-O-Sperse A205	84
Hostafon 5032	3
Zonyl FSN	6

The above coated material was subsequently coated with Hydrosil® 2627, an aqueous oligomeric aminosilane solution, and dried at 145 °F (~63 °C) to yield a coated coverage of 5 mg/ft².

The recording elements prepared according to examples 1-13, above, were each imaged by means of a commercially available thermal printer, Model VP-3500, sold by Seikosha America, Inc., Mahwah, NJ. The % haze, the scratch resistance, and the amount of crazing were determined for each film. The results are recorded in Table 1.

The haze measurements were determined using a Spectrogard II Spectrophotometer made by Gardner-Neotec Instruments, Silver Spring, Maryland.

Scratch resistance was determined by the resistance of each image to fingernail scratching. "Excellent" describes those images where no scratching was observed; "good" describes those images where scratching was observed, but it had no detrimental impact on image quality; "poor" describes those printed images that were very susceptible to scratching and the scratching was detrimental to image quality; and "fair" describes films whose scratch resistance fell between the good and poor films.

Crazing was ascertained visually. Crazing occurs upon drying of the topcoat after it has been coated on the color-forming layer and is, therefore, present before imaging. "High" describes those recorded images that were extremely crazed and "low" describes those recorded images where the image appeared substantially craze-free.

TABLE I

Example	%Haze	Scratch Resistance	Crazing
1	4.2	good	low
2	4.5	good	low
3	4.5	good	low
4	3.6	good	low
5	4.0	excellent	low
6	11.8	excellent	high
7	5.5	poor	low
8	7.7	good	high
9	7.3	poor	low
10	6.5	fair	low
11	9.0	excellent	low
12	8.0	excellent	low
13	9.3	excellent	low

As can be seen from the results shown in Table I, the thermographic recording films of Examples 1-5 according to the present invention were superior overall to comparative Examples 6-9 which employed only one silica of specified average particle diameter in the topcoat formulation. Examples 11-13 were superior in terms of scratch resistance (fingernail) and crazing, although the haze was higher for these examples which utilized fumed colloidal silica when compared with other topcoat formulations according to the present invention.

When only very small silica was used, as in examples 6 and 8 (average silica particle diameter of 5 nm), the crazing was extremely high and there was an increased level of haze. It should be noted that the presence of crazing increases the level of measured haze.

Where only silica having an average particle diameter of 20 nm was employed, as in Example 7, the recorded image was susceptible to scratching and the haze was slightly greater than for the topcoats according to the present invention.

When only silica having an average particle diameter of 100 nm was employed, as in Example 9, the recorded image was very susceptible to scratching and the haze was greater than for the recorded images of examples 1-5.

When a mixture of silicas was employed in the topcoat formulation and the largest silica had an average particle diameter of 100 nm, as in Example 10, the resulting film had less scratch resistance than the topcoats according to this invention and the haze was higher than examples 1-5 according to the present invention.

Where fumed colloidal silica and/or an organofunctional silane was employed, as in examples 5 and 11-13, the recorded image was very resistant to fingernail scratching while also being substantially free of crazing.

When an organofunctional silane was added to the topcoats of this invention, as exemplified in examples 5, 12 and 13, the thermal printhead was substantially free of head build-up after printing.

Inorganic silica films comprising mixtures of silicas such as disclosed in U.S. Patent No. 2,956,958 and described in Iler, R.K., The Chemistry of Silica, John Wiley & Sons, NY, 1979, particularly at pp. 369-371, which require 1 part silica having an average particle diameter larger than 50 nm with the average particle diameter in the range from 50 to 150 nm, would have higher levels of haze and/or be more susceptible to scratching than the topcoats of the present invention.

Since certain changes may be made in the above subject matter without departing from the spirit and scope of the invention herein involved, it is intended that all matter contained in the above description and the accompanying examples be interpreted as illustrative and not in any limiting sense.

Claims

1. A transparent thermographic recording film comprising a transparent support characterized by carrying:
 - (a) a dye image-forming system comprising a di- or triarylmethane thiolactone dye precursor, an organic silver salt, a heat-fusible organic acidic material, and polyvinylbutyral as the binder; and,
 - (b) a protective topcoat layer positioned above said dye image-forming system and comprising a water-insoluble polymeric binder, a mixture of at least two colloidal silicas having different average

particle diameters in the proportion, by weight, of 1 part of larger silica having an average diameter of 50 nm or smaller and 0.3 to 1 part of silica particles having an average diameter no more than 40% of the larger sized silica particles, the ratio of total silica to binder being at least 3 parts per weight silica to 1 part per weight binder.

- 5 2. A thermographic recording film according to claim 1 characterized in that the largest of the silica particles has an average diameter of 50 nm.
- 10 3. A thermographic recording film according to either of the preceding claims characterized in that the organic silver salt, polymeric binder and heat-fusible organic acidic material are carried in a layer on the transparent support and the di- or triarylmethane thiolactone dye precursor is in the same or an adjacent layer.
- 15 4. A thermographic recording film according to any one of the preceding claims characterized in that the protective topcoat further comprises a lubricating agent, preferably polytetrafluoroethylene.
- 20 5. A thermographic recording film according to any one of the preceding claims characterized in that the protective topcoat further comprises a surfactant, preferably selected from a nonionic surfactant or a nonionic fluoro surfactant.
- 25 6. A thermographic recording film according to any one of the preceding claims characterized in that the water-insoluble polymeric binder for the protective topcoat layer is an aliphatic polyurethane.
7. A thermographic recording film according to any one of the preceding claims characterized in that the topcoat further comprises a second water-insoluble polymeric binder.
- 30 8. A thermographic recording film according to any one of the preceding claims characterized in that the silica to binder ratio is no greater than 15:1 and preferably is from 4:1 to 6:1.
- 35 9. A thermographic recording film according to any one of the preceding claims characterized in that the topcoat comprises a mixture of 3 different sized silica particles in the proportion by weight of 1 part of larger silica particles having an average diameter of 50 nm or smaller, and 0.2 to 0.6 part of silica particles having an average diameter no more than 40% of the larger sized particles, and 0.2 to 0.6 part of silica particles having an average diameter of no more than 8 nm.
- 40 10. A thermographic recording film according to claim 9 characterized in that the topcoat comprises a mixture of 1 part silica having an average diameter of 50 nm, 0.6 part of silica having an average diameter of 20 nm and 0.6 part of silica having an average diameter of 5 nm.
- 45 11. A thermographic recording film according to any one of the preceding claims characterized in that the organic silver salt is silver behenate.
12. A thermographic recording film according to any one of the preceding claims characterized in that the heat-fusible organic acidic material is 3,5-dihydroxybenzoic acid.
- 50 13. A thermographic recording film according to any one of the preceding claims characterized in that the dye image-forming system further comprises a second heat-fusible organic acidic material.
14. A thermographic recording film according to any one of the preceding claims characterized in that one of the colloidal silicas is a fumed colloidal silica having an average particle diameter in the range of 14 nm to 30 nm.
- 55 15. A thermographic recording film according to claim 14 characterized in that the smallest colloidal silica is a colloidal silica having an average particle diameter of 5 nm.
16. A thermographic recording film according to any one of the preceding claims characterized in that the protective topcoat additionally comprises an organofunctional silane.

17. A thermographic recording film according to any one of claims 1 to 15 characterized by additionally comprising a layer of an organofunctional silane on top of the protective topcoat layer.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 0926

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4 682 192 (MASAHARU NOMURA ET AL) * column 1, line 54 - column 2, line 8; claims *	1-14	B41M5/40
Y	US-A-4 415 627 (MASAHIRO MIYAUCHI ET AL) * column 2, line 57 - line 69 *	1-14	
D,Y	GB-A-2 196 142 (FUJI PHOTO FILM CO) * the whole document * & US-A-4 820 682	1-14	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 381 (M-752)(3228) 12 October 1988 & JP-A-63 132 087 (MITSUBISHI PAPER MILLS LTD) * abstract *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 267 (M-840)(3615) 20 June 1989 & JP-A-10 69 384 (FUJI PHOTO FILM CO LTD) * abstract *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D,A	US-A-4 904 572 (DOMBROWSKI E.J. JR & KING P.F.) * the whole document *	1	B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01 OCTOBER 1992	Examiner Martine LUDI
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

EPO FORM 1501 03.82 (P0401)